

CATALYST TESTING OF HIGHLY DISPERSED METAL NANOPARTICLES FOR COAL LIQUEFACTION AND COAL/WASTE COPROCESSING

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ABSTRACT

The objective of this work is to synthesize colloidal sized dispersed metal, metal oxide, and metal sulfide clusters for applications in catalysis. We are studying metal particles in a size range of 1-10 nm in diameter. In this size range, high activities are achieved due to ultra-high surface areas. Also, product selectivity is controlled, because activity on corner and edge sites dominate with decreasing particle size. We are studying the formation of clusters in microemulsions. The procedure offers particle size control, composition control, organic phase stabilization, and particle manipulation to form catalysts of varying morphology. The procedure is especially pertinent in coal liquefaction. Catalytic dissolution activity in liquefaction depends primarily on the dispersion (catalyst/coal contact) and metal composition. Metal particles in microemulsions offer high dispersions, because of ultra-small sizes and because organic phase stabilization allows facile absorption into the coal. In addition, a variety of compositionally important species such as Fe based and Mo based materials are formed.

In the past, we have studied the synthesis and characterization of zero valence Fe and FeS₂ (pyrite) powders. We established the unique chemistry occurring in reduction and sulfiding reactions in microemulsion solvents and determined particle stability against oxidation. Zero valence Fe and FeS₂ (pyrite) powders were studied as catalysts in coal liquefaction and model liquefaction reactions such as pyrene hydrogenation and naphthyl bibenzyl methane hydrogenolysis. Best results were obtained for surfactant free FeS₂ powders showing high selectivity for low molecular weight dissolution fractions.

More recently, we have studied the formation of highly dispersed heterogeneous catalysts formed via a microemulsion / sol-gel synthesis. A two-step sequential reduction of an Fe salt followed by hydrolysis and condensation of silicon or aluminum alkoxides in a microemulsion forms nanoparticles in a silica or alumina gel. The 'ship in a bottle' approach offers extended thermal stability as the nanoparticles are sterically trapped in the micropores of the gel. The advantages of the microemulsion technique are retained with the added advantages of surfactant removal and thermal stability. The highly dispersed heterogeneous catalysts are ideal for coal / waste coprocessing. The catalysts are bifunctional; the highly dispersed metals act as coal hydrogenation catalysts, and the silica or alumina support depolymerizes the plastic waste. Initial results indicate the metal strongly influences high molecular weight dissolution products, and the support influences low molecular weight heptane soluble fractions.

INTRODUCTION

Colloidal sized metal and semiconductor particles with diameters of 1 - 20 nm (nanoclusters) are of current interest because they mark a material transition range between molecular and bulk properties. With decreasing colloid size, bulk properties are lost as the continuum of electronic states breaks down (i.e. quantum size effects) and as the fraction of surface atoms becomes large. A common nanocluster

synthesis technique is the reduction of metal salts in inverse micelle solutions. Inverse micelles are solution structures formed by the self-assembly of surfactants in apolar solvents (i.e. toluene, alkanes). Surfactants possess two distinct moieties, a hydrophilic head group and a hydrophobic tail group, and they self-assemble in apolar solvents so that the hydrophilic head groups shield themselves from the oleic surroundings. The relatively polar head group regions solubilize and confine added metal salts and act as reaction cages when a reducing agent is introduced. Ultra-small, monodispersed particles sterically stabilized in solution by surfactant are formed. The materials are treated as pseudo-homogeneous catalysts. Advantages of the inverse micelle synthesis technique include mean particle size control and compositional variety. Particle size control results from regulation of the nucleation site size (inverse micelle size) and the particle growth rate (material exchange rate between inverse micelles). A variety of metals and bimetallics are produced by choosing different metals salts and mixtures of metal salts.

In order to isolate nanoclusters and preserve their unique properties without the presence of any stabilizing agents that attach to the particle surface, we have developed sol-gel processing in inverse micelle, nanocluster solutions to encapsulate or sterically entrap nanoclusters in the micropores of xerogels and aerogels. The synthesis is a sequential reduction of a metal salt and sol-gel processing of an added siloxane precursor in an inverse micelle solution. Sol-gel processing of porous silica gels in polar solvents has been used to encapsulate a variety of large molecules including laser dyes, photochromics, and proteins. Sol-gel encapsulation involves polymerization of a gel precursor, usually tetramethoxysilane or tetraethoxysilane, to build the silica gel structure (host) around the dopant (guest). Steric entrapment occurs when the gel pore size is comparable to the dopant size. The product of this work includes nanoclusters in a silica matrix that remain small, of one size, and highly dispersed even after the removal of the surfactant.

The pseudo-homogeneous catalysts prepared here are especially pertinent in coal liquefaction. Catalytic dissolution activity in liquefaction depends primarily on the dispersion (catalyst/coal contact) and metal composition. Metal particles in microemulsions offer high dispersions, because of their ultra-small size and because organic phase stabilization allows facile absorption into the coal. In addition, a variety of compositionally important species such as Fe based and Mo based materials are formed. We have studied the synthesis in inverse micelles and characterization of Fe based clusters. The materials have been tested as catalysts in coal liquefaction, pyrene hydrogenation, and naphthyl bibenzyl methane hydrogenolysis. Reduction of Fe salts in inverse micelles leads to the formation of mixtures of FeB and α -Fe. Reaction with a sulfiding agent produces FeS₂ (pyrite). Pyrite powder is most active in coal liquefaction and hydrogenolysis reactions showing high selectivity for oil fractions (50% of total conversions). In all cases the activity is limited both sterically and chemically by the presence of surfactant.

The Federal Energy Technology Center is conducting a focused technology development program to study coal - waste coprocessing to produce liquid fuels. In the area of coal - plastic coprocessing, results to date are mixed. Potential problems include the thermal degradation difference between coal and plastic. Thermal degradation of coal occurs at 400°C while commingled waste plastic breaks down at 430°C. Immediately, higher processing temperatures are required. In addition, coal and plastics are not good co-solvents; coal is highly aromatic and plastics are largely aliphatic. To overcome the problems, researchers have suggested using two-stage reactions, resid as a co-solvent, and mixtures of catalysts serving two functions. The highly dispersed heterogeneous catalysts successfully combine the hydrogenation functionality of Fe based particles with the cracking functionality of SiO₂/Al₂O₃ mixtures serving as a mixture of two catalysts. Initial results indicate the metal strongly influences high molecular weight dissolution products, and the support influences low molecular weight heptane soluble fractions. The

ultimate goal will be to develop plastic as a hydrogen source to increase the economic viability of coal liquefaction in a simple, single stage, single catalyst process.

EXPERIMENTAL

Materials: The surfactant didodecyldimethylammonium bromide (DDAB), apolar solvent toluene (99.9+% purity), reducing agent lithium borohydride in tetrahydrofuran (2M), gold trichloride, tetraethylorthosilicate (TEOS), and a 40 wt. % tetrabutylammonium hydroxide (TBAOH) in water solution were purchased from Aldrich and used as delivered. Polydiethoxy siloxane (M.W. = 610 gm/mol), an oligomer of TEOS formed by a proprietary pre-hydrolysis reaction, was purchased from United Chemical Technologies of Bristol, PA and used as delivered. Hexanol is used as a washing solvent and is purchased from Aldrich at 99.9+% purity.

Synthesis of Fe and FeS₂ Pseudo-Homogeneous Catalysts: The synthesis technique is general and specific samples differ only in the type and concentration of salts and surfactant added to the apolar solvents. First, the inverse micelle solutions are prepared by adding surfactant to the solvents (i.e. DDAB in toluene, C₁₂E₄ in octane). Then, the metal salts are introduced and the precursor salt solutions are mixed overnight on a stirring plate to assure complete solubilization. Transparent yellow Fe salt solutions are formed. To form metallic Fe, 2M LiBH₄/THF solution is directly injected into the salt solutions under rapid stirring to initiate the reduction of iron. The reaction is run at a 5:1 molar ratio of [BH₄⁻]:[Fe³⁺]. Fe solutions immediately turn clear and transparent or black. To form FeS₂, 1M Li₂S/H₂O is injected into the salt precursor solutions at a 5:1 molar ratio of [S₂²⁻]:[Fe³⁺]. The solutions turn dark green upon reaction. To produce powders from the solutions, 15 vol. % methanol is added to the particle solution. After several hours a black or green precipitate is formed at the bottom of the flask below a clear and transparent solution. The precipitate is separated from the solution by centrifugation and washed with methanol. The process is repeated two or three times, and the powder was finally dried. All reactions and sample manipulations are carried out under dry, oxygen-free conditions.

Synthesis of Highly Dispersed Heterogeneous Catalysts: Surfactant (1-5 wt. %) is added to toluene and stirred by hand shaking to form the inverse micelle solution. FeCl₃ (0.001M) and the gel precursor (0.4M) are added, and the solution is stirred until the salt is fully solubilized. A yellow colored transparent solution is formed. The LiBH₄/THF solution is injected into the salt precursor solution under rapid stirring so that the [BH₄⁻] : [Fe³⁺] = 3:1. The Fe solution immediately turns dark black. The 40 wt. % TBAOH in water solution is added 1 to 5 minutes afterwards, and gelation time is marked when the solution no longer flows under gravity. A dark black, viscous gel is formed. The water to gel precursor molar ratio ranges from 1:1 to 4:1. The gels are dried at 50°C overnight in air and then are calcined at 450°C in flowing air for 2 hours. The synthesis has been extended to form alumina and silica/alumina mixture supports, and is currently being extended to include the formation of FeOOH and FeS₂ particles.

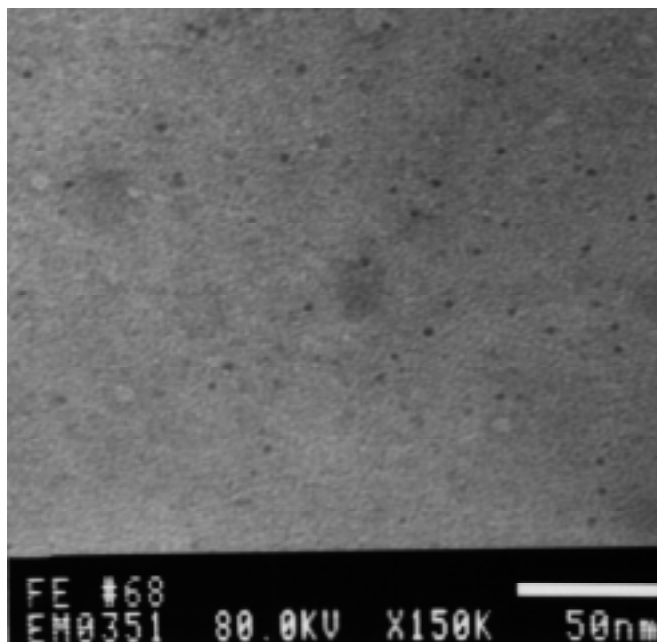
Coal Liquefaction Catalyst Testing: Microbatch reactors are loaded with 1.67 gm coal (DECS-17 Blind Canyon: 3.74% moisture, 0.36% iron, 0.02% pyritic sulfur, 7.34% mineral matter), 3.34 gm phenanthrene, and 1 wt. % catalyst loading on a metal basis. Reactors are charged to 800 psig cold H₂, and reactions are run in sand baths at 400°C for 1 hour. Reaction products are rinsed out of the reactors with THF. Product analysis consists of sequential solubilization in THF and heptane to determine asphaltene and pre-asphaltene fractions, and oil fractions. Elemental sulfur is added.

RESULTS AND DISCUSSION

Transmission electron micrographs of Fe and FeS₂ particles show ultra-small particles of uniform size and shape highly dispersed on the grid (Figure 1). The number average diameter by TEM of metallic Fe and FeS₂ is 1.5 +/- 0.2 nm and 3.1 +/- 0.1 nm, respectively. Methanol extracted Fe powder has been characterized by TEM and BET surface analysis. TEM pictures show agglomeration of the highly dispersed particles. Large agglomeration structures approximately 100 nm in size are observed. These structures consist of the ultra small Fe particles (approximately 2 nm in diameter) flocculated together. Multi-point BET analysis gives a surface area of 156 m²/gm for this sample.

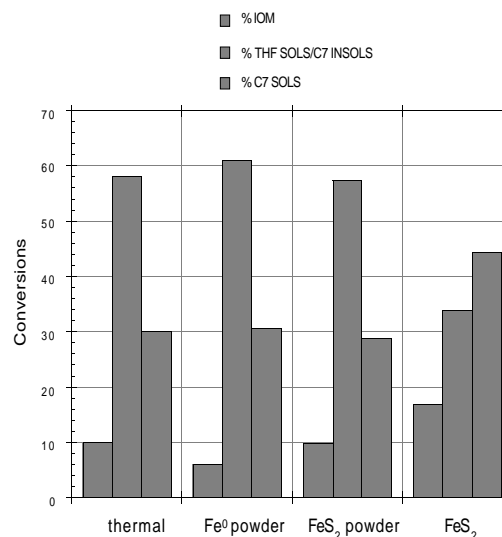
Mossbauer spectroscopy completed on an *in-situ* sample frozen at -176°C indicates the presence of three different forms of iron. The spectrum is fit with two doublets and a singlet. We assign the first doublet to the presence of fine superparamagnetic particles of FeB, the second doublet to the presence of Fe²⁺BO_x, and the singlet to the presence of superparamagnetic Fe metal. On the basis of spectral areas, the iron phases are present at 83, 15, and 2 mole %, respectively with the species order listed above.

Selected area electron diffraction patterns of *in-situ* iron particles deposited on the microscope grid are consistent with the presence of α -Fe. The ratios of theoretical diffraction parameters to the first diffraction parameter (d/d_1) are known for many crystalline materials. The diffraction pattern of Fe shows several maxima, and experimentally we observe d/d_1 equal to 1, 0.701, 0.573, 0.482, 0.436, and 0.381. Theoretical values of d/d_1 for α -Fe equal 1, 0.707, 0.577, 0.500, 0.447, and 0.408. Theoretical values of d/d_1 for FeB equal 1, 0.842, 0.728, 0.696, 0.670, and 0.615. The electron diffraction results, therefore, indicate the presence of α -Fe and do not indicate the presence of any crystalline iron oxides, borides, or borates. A separate diffraction pattern consistent with the presence of crystalline B₂O₃ as a reaction by-product is also detected.



It has been reported that the presence of air during the reduction process favors the formation of metallic metal over metal borides by the following mechanism: $MB + O_2 \rightarrow M(s) + B_2O_3$. In our procedure, the reaction is done in an argon environment, but the TEM grid is exposed to air prior to microscopy. The above stated mechanism is most likely responsible for the detection of α -Fe as the majority phase by electron diffraction while FeB is the majority phase detected by Mossbauer. The detection of crystalline B₂O₃ by diffraction supports this theory.

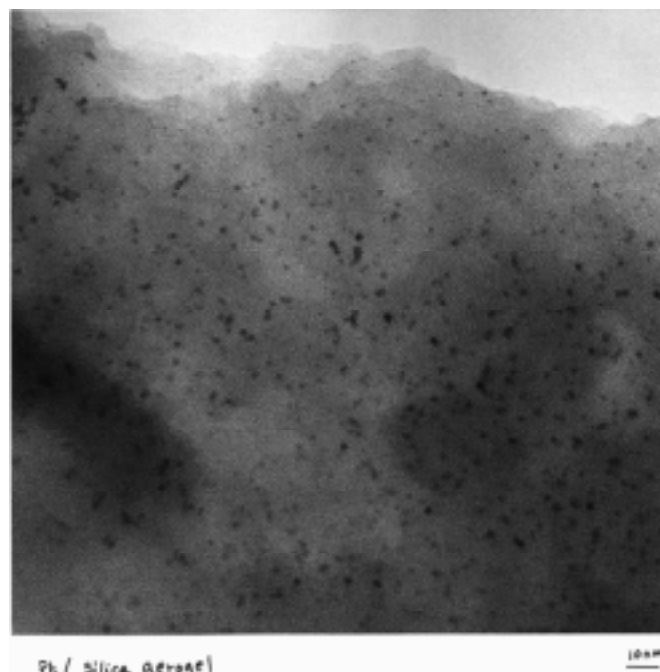
Iron sulfide has been studied extensively as a coal liquefaction catalyst. It is believed that pyrrhotite (Fe_{1-x}S) is the active form of the iron catalyst, and that pyrite is reduced to pyrrhotite under liquefaction conditions. We have attempted to use our Fe and FeS_2 (pyrite) particles as coal liquefaction catalysts. Fe and FeS_2 powders with surfactant show no improvement over thermal reactions. Liquefaction is highly dependent on a hydrogen donating solvent and surfactant pyrolysis by-products may scavenge hydrogen. Surfactant free FeS_2 powder shows a decrease in the overall conversion to organic products, but an actual increase in the amount of low molecular weight organic products. High IOM percentages may be due to high selectivity for cracking polar functionalities within DECS-17.



Transmission electron micrographs of highly dispersed heterogeneous catalysts formed via a microemulsion / sol-gel synthesis show ultra-small particles of uniform size and shape highly dispersed in the silica. Particle diameter on average is 5.1 nm. Particle size is tested as a function of reaction stoichiometry, the gel precursor type, the drying procedure, and washed vs. unwashed samples. Particle size is independent of reaction stoichiometry, gel precursor type, and the effect of washing. For washed samples, particle size is independent of the drying procedure (xerogels vs. aerogels).

The effect of calcination on particle size, aggregation, and support surface areas and morphology has been determined. In uncalcined samples, the particles are approximately 5 nm in diameter, highly dispersed, and monodispersed in size distribution. After calcination, the particles are larger (7 nm in diameter), less monodispersed, but still fairly distributed. The effect of particle sintering appears small in these materials.

Support surface areas increase by an order of magnitude upon calcination. Calcination is often used to remove organic and other residuals from the support at the cost of losing microporosity. In supports synthesized by sol-gel methods, these residuals include water, ethanol, terminal and unreacted alkoxy groups. In the case of our synthesis, the primary organic residual is unreacted alkoxy groups and surfactant (DDAB). Removal of these groups upon calcination is the likely reason for increased support surface area.

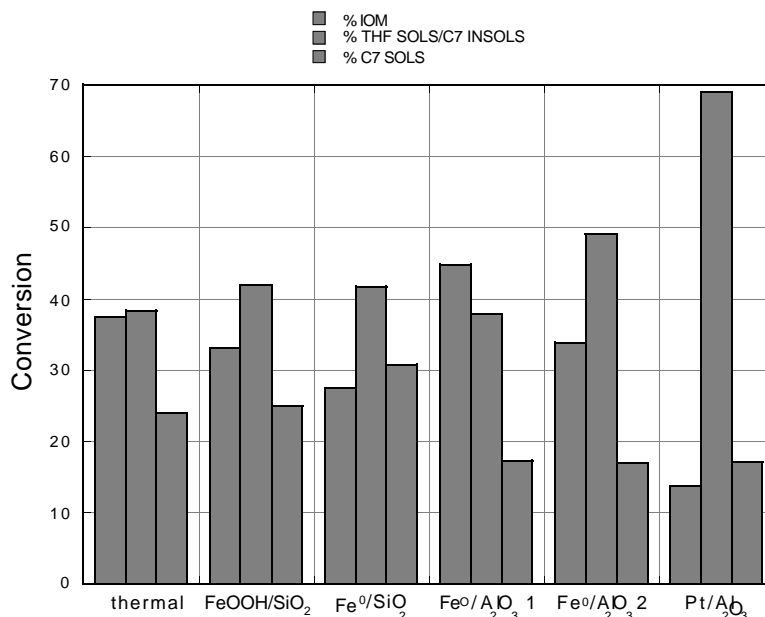


We have completed initial coal liquefaction catalyst testing with the highly dispersed heterogeneous materials. The ultimate goal will be to develop plastic as a hydrogen source to increase the economic viability of coal liquefaction in a simple, single stage, single catalyst process. The highly dispersed heterogeneous catalysts are ideal for coal / plastic coprocessing, because they are bifunctional. The dispersed metal acts to hydrogenate the coal, and the silica or alumina support depolymerizes the plastic waste.

Results of the initial liquefaction tests are shown below. There are two trends that are important. First, overall conversion increases markedly with platinum. Strong effects on metal type indicate that despite being embedded in the support the metal is still highly dispersed with respect to the coal. Iron based materials are far less active than platinum. The second important result is that Al_2O_3 as a support consistently shows lower conversion to oil fractions than thermal runs. Al_2O_3 is a far better cracking catalyst than SiO_2 due to surface acidity. We believe that cracking is occurring at a much faster rate than hydrogenation with Al_2O_3 causing regressive reactions with the coal. A support mixture of SiO_2 and Al_2O_3 could be used to balance the hydrogenation and cracking rates to optimize conversion.

Metallic iron shows only an increase of roughly 7-10% in overall conversion compared to thermal. We are currently preparing FeOOH and FeS_2 for testing in the heterogeneous recipes. It is stated in the results below that FeOOH was tested. A nominal recipe for FeOOH was attempted, but characterization does not indicate the presence of FeOOH . The recipe must be adjusted further to the inverse micelle technique. FeS_2 formation has been completed, but testing is not available yet.

Finally, two different $\text{Fe}/\text{Al}_2\text{O}_3$ samples are shown in the results below. In the first as described in the experimental section, a two-step sequential reduction of an Fe salt followed by hydrolysis and condensation of aluminum alkoxides in a microemulsion forms nanoparticles in an alumina gel. In the second synthesis technique, nanoparticles and gels are formed in separate flasks, and the clusters are allowed to diffuse into the gel micropores upon mixing. Steric entrapment and thermal stability result from controlled drying and structural collapse of the gel. This latter methodology is currently being developed further.



CONCLUSIONS

Inverse micelles have been used to synthesize 1-10 nm in diameter metal, metal oxide, and metal sulfide particles. The synthesis provides pseudo-homogeneous catalysts or is combined with sol-gel processing to form heterogeneous materials. Fe based materials have been developed for direct coal liquefaction, and FeS₂ shows high selectivity for conversion to oil fractions. The heterogeneous materials are being developed as coal / plastic coprocessing catalysts, because they are bifunctional potentially providing a simply, single stage, single catalyst process. The dispersed metal acts to hydrogenate the coal, and the silica or alumina support depolymerizes the plastic waste. Initial coal liquefaction tests have demonstrated the hydrogenation and cracking capabilities and have suggested how the materials may be tuned to optimize conversion.

SELECTED PUBLICATIONS

1. Martino, A., Stoker, M., Hicks, M., Bartholomew, C.H., Sault, A.G., Kawola, J.S., "The Synthesis and Characterization of Iron Colloid Catalysts in Inverse Micelle Solutions", *Applied Catalysis*, in press.
2. Martino, A., Yamanaka, S.A., Kawola, J.S., Loy, D.A., Encapsulation of Gold Nanoclusters in Silica Materials via an Inverse Micelle / Sol-Gel Synthesis, *Chem. Mater.*, **9**(2), 423, (1997).
3. Martino, A., Wilcoxon, J.P., Kawola, J.S., Synthesis and Characterization of Coal Liquefaction Catalysts in Inverse Micelles, *Energy & Fuels*, **8**(6), 1289, (1994).